Organic Matter, Decomposition

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Glossary

Cellulose $\beta[1-4]$ polymer of glucose that forms the rigid support of plant cell walls
Decomposition rate Speed of decomposition of particular organic compounds; in the first-order kinetics used in this article, expressed as the fractional loss of a substance per unit time (e.g., $days^{-1}$)
Humus Dark-colored organic by-products of decomposition consisting of microbial cell walls and other resistant forms produced by free-radical reactions of sugars, amino acids, and lignin breakdown products; closely associated with soil mineral particles
Isotope Chemical elements with the same atomic number and position in the periodic table and, thus, with nearly identical chemical behavior but differing mass
Lignin Amorphous cementing agent of plant cell walls; together with cellulose and hemicellulose, provides the woody, rigid structure of plants; comprised of a series of aromatic rings joined by three carbon side chains
Mathematical model System of equations describing a related series of pools, or quantities of materials, and the rates of transfer between them; the speed of reactions are usually defined as a reaction rate
Microbial biomass Total amount, expressed as either dry weight or carbon, of the microorganisms in soil
Organic matter Mixture of unidentifiable, partially decayed plant and animal residues, microbial bodies, and the waste products of decomposition, or humus

DECOMPOSITION is defined as the process of separation of materials into their constituent parts. Organic matter, in turn, relates to those materials derived from living organisms. Decomposition of organic matter, therefore, represents the biodegradation of the organic materials, originally derived from living organisms to their constituents of carbon dioxide, water, and other nutrients such as nitrogen and phosphorus. The oxidation of organic materials to release the energy of the sun originally stored during the photosynthetic reaction by the reduction of CO_2 to organic materials is the driving force behind life. During the photosynthesis process, CO_2 is reduced and a large amount of energy is stored in thermodynamic terms. Decomposition, as a reverse of this process, lowers the free energy of the substrates. A true understanding of the decomposition process, therefore, involves a knowledge of the thermodynamics involved. Those forms depending on the oxidation of organic materials for energy are known as heterotrophs. This decomposition completes the carbon cycle initiated during photosynthesis. A few organisms, the chemoautotrophs (also known as chemolithotrophs), can derive their energy by oxidizing reduced compounds other than those found in organic matter. Often they can also reduce CO_2 directly to cell constituents and thus do not require organic substrates for the building of these constituents. These organisms, like the more commonly recognized phototrophic plants, are thus a portion of the primary production rather than the decomposition phase of life.

The greatest amount of heterotrophic decomposition is carried out by microorganisms. In ecological studies, they often are known as decom-

posers. Other heterotrophic life forms such as vertebrates and invertebrates (fauna) usually feed on the soluble sugars, starches, and proteins of plants, on each other, or on waste products such as manures. The fauna account for 10–30% of decomposition on a global basis. Where dominant, such as in the case of large animal grazers or termites, they can play major roles in decomposition. They also provide mixing and population control functions. Humans are rapidly becoming the major biological influence on this planet. They concentrate nutrients in cities and thus cause pollution and eutrophication. Their activities also cause major disturbances such as land-clearing and the reintroduction of carbon that was stored in fossil fuels over geological time. [*See* HETEROTROPHIC MICROORGANISMS.]

For heterotrophic organisms to gain the energy stored in plant or animal substrates, the degradative reactions must be enzyme-mediated coupled to the energy-capturing mechanisms of life. This is composed of coupled oxidation reduction reactions involving the transfer of electrons from a reduced substrate to a more oxidized electron acceptor. Elemental oxygen is the most common electron acceptor in the process of decomposition. Its use also allows the capture of the largest amount of energy. Other electron acceptors can act in the absence of O_2. These include organics in the fermentation process, oxidized nitrogen such as NO_3, NO_2, NH_2OH, and NO, oxidized metals such as Fe^{3+} and Mn^{4+}, oxidized sulfur such as SO_4^{2-}, $S_2O_3^{2-}$, and even CO_2.

Seldom are CO_2 and H_2O the only products of decomposition. Some of the substrate is incorporated into new cell materials. In addition, amounts of waste products are almost always extensive. These involve an extensive number of secondary products with various degrees of resistance to further degradation. Decomposition occurs on the surface and within the soil, in lakes and streams and in sediments. The microorganisms are so small that they are not readily separated from the decaying vegetation or from the soil and sediments where most decomposition occurs. Organic matter by definition, therefore, consists of the partially decayed plant residues that are no longer recognizable as plant materials, the microorganisms and some of the small fauna involved in decomposition, and the by-products of decomposition. These by-products undergo a process called humification to form the material known as humus. Humus consists of dark-colored, organic materials that have a higher carbon and lower oxygen content than most life forms. They are approximately 50–55% carbon, 4.5% nitrogen, and 1% sulfur, with varying amounts of phosphorus and metals. These materials are very closely associated with the soil inorganic constituents and decompose only very slowly, accumulating in nature as soil organic matter, peats, coals, oils, and organic sediments. The process of decomposition of plant residues by microorganisms with the production of by-products, the interaction with the soil colloids, and the humification process is shown in Fig. 1. [*See* BIODEGRADATION.]

I. The Substrates of Decomposition

The great interest in the role of plant and soil organic matter decomposition as factors affecting global climate change has consolidated information on the relative amounts of substrates in the many different areas of the world. Table I shows the carbon in the plant biomass relative to the carbon in aboveground plant litter fall for some of the major climatic areas of the world. In presenting averages such as these, it should be recognized that any one vegetation type has a great range of values. Tropical forests cover the largest single land area and contain the largest amount of plant biomass per unit of land area. These are followed in both area and amount of plant biomass by temperate and boreal forests. Savannahs, which are grasslands interspersed with trees, represent a significant land area. They do not have as

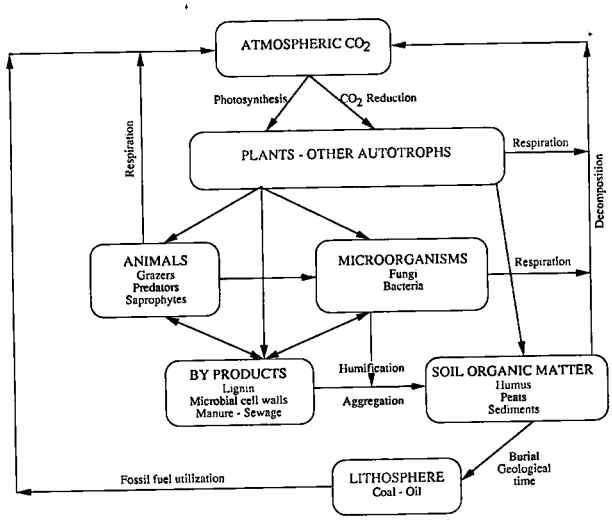

Figure 1 The role of living organisms in the production of waste products during the decomposition of organic matter.

large a plant biomass but still represent a significant input into a very large soil organic matter pool. Agricultural soils are interspersed throughout all of the major vegetation types and are not shown in Table I. They represent approximately 10% of the global soil surface area. Humans have, however, altered a much larger percentage than this.

Generally, only a small proportion of the plant primary production is harvested, except in some agricultural soils. In these soils, the amount of residues available for decomposition is often lower than that shown for the noncultivated vegetation types. Information on underground production from roots is not yet available for many areas of the world. Where measurements have been made, it has been found that 30–50% of the total plant production is transported underground. Some of this is directly respired to CO_2 by the root system. Root exudates, sloughed materials, carbon translocated to microbial symbionts, and root turnover supply significant substrates for decomposition. In many cases, this exceeds the substrate entering via litter fall.

In steady-state situations, dividing the amount of soil organic matter by the annual litter input gives an estimate of turnover time. This shows the effect of climate on decomposition. In Table I, we do not have an estimate of aboveground litter accumulating on the forest floor, nor do we have measurements of underground production; however, the ratio of soil carbon to annual litter input still gives us a good relative measure of decomposition times. The soil organic matter of tropical forests represents a total that is 7 times the annual litter fall, whereas in a grassland soil the accumulated organic matter is shown to be 34 times as great as the annual litter fall. In the tundra, the carbon in the annual litter fall represents only $\frac{1}{300}$th that of the soil carbon stored in the surface meter. This shows the relative accumulation of organic matter in the soil profile and is an indicator of the rates of decomposition of soil organic matter.

The global carbon reservoirs in Table II show that the atmosphere represents a small portion of the global carbon reserves. Atmospheric carbon is slightly greater than the plant biomass, but only one-half that of the soil humus. However, as demonstrated by the present climate change problems where a doubling of the atmospheric CO_2 will result in significant temperature and sea-level changes, the atmosphere is very sensitive to small changes in annual fluxes. On an annual basis, decomposition is nearly equivalent to photosynthesis. On land, this is approximately 110×10^{15} g annually. Oceanic decomposition is estimated to be approximately one-half of terrestial. However, the large accumulation of organic carbon in soil humus, the dissolved organic carbon of the ocean, and the huge concentrations in the lithosphere show that over geological time photosynthesis has been greater than decomposition. Humans are presently exploiting this stored fossil carbon. Although <0.1% of the huge carbon reserves accumulated in the lithosphere over geological time are presently exploitable, the emission of CO_2 into the atmosphere via the burning of fossil fuels and via land-clearing has resulted in the >100 ppm change in CO_2 (between 1850 and 1990) shown in Table II.

Because soil organic matter and plant litter together comprise the majority of decomposable substrates, the remainder of this discussion will concen-

Table I Plant Biomass, Input of Litter to Soil, Soil Organic Matter, and Microbial Biomass of Major Global Vegetation Types

	Tropical forest	Savannah	Temperate forest	Temperate grassland	Boreal forest	Tundra
Area (10^{12} m^2)	24.5	15	12.5	9	12.0	8
Carbon in plant biomass (kg m^{-2})	18	1.8	14	1.4	9	0.25
Carbon in aboveground litter fall (kg m^2 yr^{-1}	1.71	0.36	0.37	0.67	0.25	0.075
Soil carbon (kg m^{-2})	13	5.4	9	23	15	22
Soil nitrogen (kg m^{-2})	0.82	0.33	0.64	2.1	1.1	1.1
Carbon in microbial biomass (g m^{-2})	50	60	110	215	35	20
Nitrogen in microbial biomass (g m^{-2})	2	8.7	14	51	2.5	1
Microbial turnover (yr)	0.07	0.17	0.30	0.32	0.14	0.27
Soil carbon litter input[7] (yr)	7	15	24	34	60	293

[Adapted from Smith, J. L., and Paul, E. A. (1990). *Soil Biochem.* **6**, 367–386. Marcel Dekker.]

Table II Global Carbon Reservoirs and Total Decomposition in the Ocean and on Land

Carbon reservoir	Organic carbon ($\times 10^{15}$ g)	Decomposition ($\times 10^{15}$ g yr^{-1})	Inorganic carbon ppm	Inorganic carbon ($\times 10^{15}$ g)
Atmosphere				
1850	—		250	560
1990	3.2		365	765
Oceans		55		37,400
Living organisms	3			
Dissolved organic carbon	1000			
Land		110		
Plant biomass	500			Various
Animals	2			
Microorganisms	3			Carbonates
Litter	90			
Humus	1500			
Lithosphere				
Recoverable fuels	10,000			Various
Nonrecoverable	16,000,000			Carbonates

[From Bolin, B., and Cook, R. B. (1983). *Scope Report* **21**, 41–65.]

trate on these materials and on the microorganisms mediating these transformations.

All organic substrates are composed of various proportions of a related series of compounds comprised primarily of carbon, hydrogen, and oxygen. Varying concentrations of nitrogen, sulfur, and phosphorus are also incorporated into the molecules. These form soluble, low-molecular weight cytoplasmic constituents and a series of higher-molecular weight constituents that include starches, hemicellulose, cellulose, lignin, nucleic acids, and proteins. The general composition of plant residues varies greatly with plant type but can be represented as shown in Table III. The sugars are combined in a number of polymers. Starch, the major food reserve of plants, is of special significance to the nutrition of animals but makes up only a small proportion of the total carbon that is returned to the soil. Hemicellulose, lipids, cellulose, lignin, and a nitrogen-containing component make up the rest of the plant materials.

II. Organisms and Enzymatic Processes Involved in Decomposition of Specific Substrates

A. Plant and Soil Carbohydrates

Higher animals are generally restricted to the degradation of starches, lipids, proteins, nucleic acids, and simple sugars. In a number of cases, the rumi-

Table III Constituents of Plant Residues Entering the Decomposition Process

Ease of decomposition	Constituent	Amount in plants (%)
Cytoplasmic constituents, readily decomposable	Amino acids–sugars	5–30
	Proteins	1–20
	Fatty acids	1–4
	Nucleic acids	1–2
Complex carbohydrates, moderately decomposable	Hemicellulose	10–30
	Cellulose	10–50
Resistant materials	Lignin	5–30
	Waxes	1–4

nants, bacteria, and protozoa within the animal's intestines carry out a fermentation that includes the degradation of otherwise insoluble plant constituents and thus benefit the host. The fauna of soils and of many aqueous systems feed directly on living plant materials (grazers), feed on other organisms or predators, or utilize the waste products or dead tissues (saprophytes). Soil fauna, such as earthworms, mites, and collembola, (1) grind plant materials so they are more accessible to microorganisms (alternatively, the clay–organic matter complexes thus formed could also slow decomposition rates), (2) mix the detritus with the soil, (3) spread microorganisms throughout the soil, and (4) prey on microbes. Predation keeps the microbial population active by releasing nutrients that would otherwise be tied up in the standing crop of microbes. Termites where they occur in tropical and subtropical soils have major effects on decomposition. Termites are usually grouped as epigeal (aboveground, often tree-dwelling) or hypogeal (underground). They are also grouped as to food sources (wood, litter, or humus) and whether or not they construct identifiable nests. The fungus-cultivating termites (Macrotermitinae) transport material underground to fungus gardens. The termites feed on the fungi and on the associated decaying vegetation. Seasonally, wet tropics of Malaysia represent some of the highest termite populations (3000–4000 m^{-2}). Of these, 15% were found to be litter feeders, 25% were classified as humus feeders, and 60% fed on wood.

Humus-feeding termites and a few tropical earthworms are the only fauna feeding on this recalcitrant substrate. The effect of litter and humus feeders lowers the soil organic matter equilibrium levels from those that would be predicted from litter inputs. The utilization by termites of lignin and humates is associated with an alkaline foregut, possibly by the production of lignolytic enzymes by the termite itself, as well as by the associated organisms in the hindgut.

Cellulose, the most abundant constituent of plant residues (Fig. 2), is associated with other compounds such as hemicellulose and lignin. It occurs in crystalline and amorphous forms with a molecular weight of about 10^6 and is composed of glucose units joined by β[1–4] linkages. The individual unbranched chains are held together by hydrogen bonds. A very large diversity of enzymes, named cellulases, occur in nature. These are produced by a variety of aerobic bacteria such as *Cellulomonas, Cellovibrio, Thermomonospora,* and *Cytophaga.* Anaerobic cellulolytic bacteria include *Acetovibrio,*

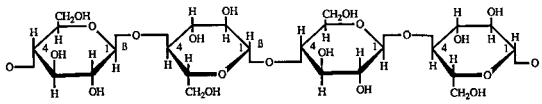

Figure 2 The structure of cellulose, a major structural component of plant cell walls.

Bacteroides, Clostridium, and *Ruminococcus.* [*See* CELLULASES.]

Cellulose is degraded by a number of fungal types. The white rot fungi degrade cellulose and are one of the few microorganisms that also degrade the more resistant lignin. The extracellular cellulases of fungi include endoglucanases, cellobiohydrolases, and β-glucosidases. The endoglucanases cannot hydrolyze crystalline cellulose but are active against amorphous cellulose and soluble derivatives. They interact with cellobiohydrolases to hydrolyze crystalline cellulose. The β-glucosidases complete the hydrolysis to glucose. Oxidative enzyme systems of white rots such as cellobiose oxidase also participate in the reaction. The oxidoreductases formed by white rots thus form a link between cellulose decomposition and lignin degradation. *Phanerochaetes chrysosporium* is probably the best-studied white rot fungi. Others include *Pleurotus* and *Coriolus.*

Fungi that break down polysaccharides associated with lignin and remove the CH_3 and R-O-CH_3 side chains leave behind phenols. These phenols on oxidation turn brown; therefore, the organisms causing this type of rot are called brown rot fungi. Organisms carrying out this type of decomposition are *Poria* and *Gloeophyllum.* Wet conditions where there is a water-substrate contact favor another group of fungi, the soft rot fungi, which can be very effective degraders of cellulose and hemicellulose. These are represented by *Fusarium solani, Penicillium funiculosum,* and *Trichoderma reesei.* The cellulose-hydrolyzing enzymes of fungi are multiforms of glycoproteins (sugar plus a protein) with sterically different end-groups and different covalently attached neutral carbohydrates. This, plus differences in the amino acid composition, accounts for the diversity of enzymes involved in these reactions.

Bacterial cellulase systems of both aerobic and anaerobic bacteria differ from the fungal cellulases by being primarily cell-bound. The bacteria attach themselves to the substrate before decomposition proceeds. They often employ a complex, multicomponent, cellulolytic organelle called a cellulosome, which attaches the bacteria to the cellulose. Anaerobic cellulose decomposition plays a major role in animal associations, in peats, and in sediments. It

also is being carefully examined relative to sewage treatment plants and in the possible commercial degradation of complex carbohydrates.

Hemicelluloses are a group of carbohydrates that are defined by being soluble in sodium hydroxide. They contain various polymers of sugars (hexoses, pentoses, and sometimes uronic acids). These comprise 10–30% of plant residues. Unless very closely associated with lignin and cellulose, they are fairly readily broken down in nature by several enzymes collectively known as pectinases. Fungi appear to initiate the attack on hemicelluloses, but actinomycetes maintain degradation over prolonged periods.

Soil carbohydrates form approximately 15% of soil organic matter, and, because there is much more soil organic matter than there is plant litter, soil carbohydrates represent a potentially larger pool of substrate than plant residues. These, however, are not easily decomposed. The polysaccharides in soil are composed of monomers quite different from those occurring in plant residues and are thus assumed to be primarily of microbial origin.

Carbohydrates form the basis, together with a nitrogen side chain, of microbial cell walls such as the chitin of fungi (Fig. 3) and the peptidoglycans of bacteria (Fig. 4). These are not as readily decomposed as the microbial cytoplasmic constituents. They represent a reserve of slowly available, potential soil nutrients. In the free state, most carbohydrates are degradable, but soil carbohydrates are resistant to attack. Absorption to clay surfaces and reactions with polyvalent cations such as iron, aluminum, and copper greatly reduce microbial decomposition. Another explanation for their persistence is the role carbohydrates play in binding individual soil particles into aggregates, which produce the structure of soil. The stability of aggregates results

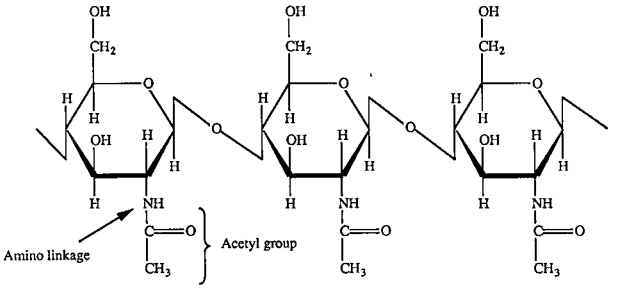

Figure 3 The structure of chitin, which is present in fungal cell walls and certain animal exoskeletons.

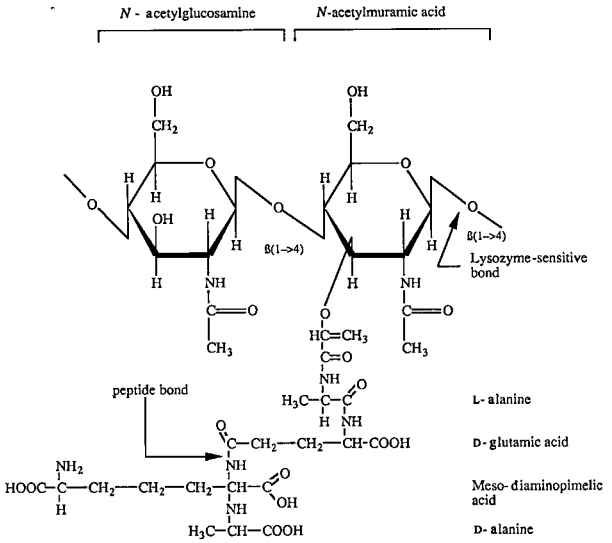

Figure 4 The structure of repeating units of peptideglycan as found in the cell walls of many bacteria.

in physical protection from microbial attack, which makes these compounds persist in soils for extended periods.

B. Lignin and Soil Humus

The lignin structure is based on an aromatic ring and a three-carbon side-chain unit (Fig. 5). Unlike starches, cellulose, and protein, lignin is not formed by a specific enzyme but, rather, by the polycondensation of the phenolic precursors of this compound in a chemical reaction that includes free radicals. The structure involves many multidimensional linkages as well as C-O-C (ether) linkages. These together with the high aromaticity make the structure very difficult to decompose. Lignin is formed together with hemicellulose as an encrusting material on the cellulose matrix of plants. It could be said to act as the concrete in reinforced cement, whereas the cellulose would be related more to the steel reinforcing bars. The combination gives plants their structural strength and resistance to decomposition. The diversity in lignin structure makes it difficult for a specific enzyme to bring about degradation. Furthermore, partial degradation products have free-radical characteristics and are very reactive. They interact with the proteinaceous enzymes required for degradation. This reaction is very similar to the tanning effect of leather. It inactivates the enzymes by the reaction with polyphenols and inhibits further attack on the substrate.

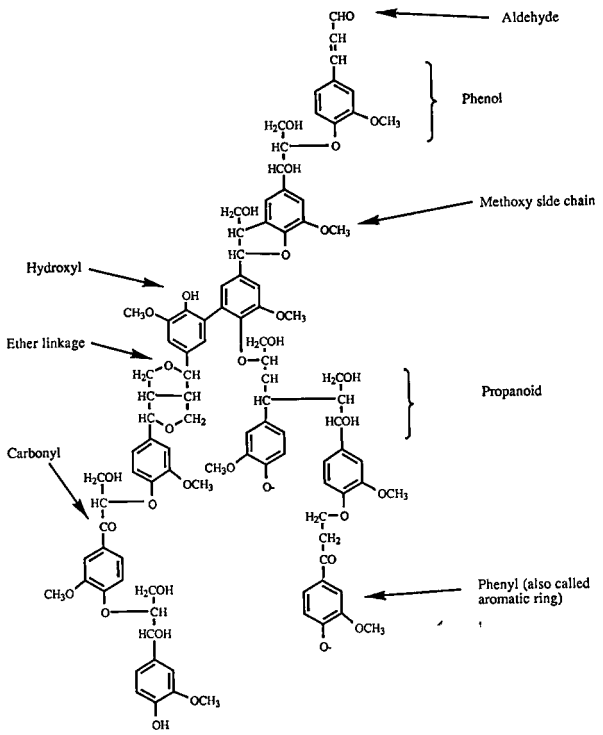

Figure 5 A representative structure showing the composition of lignin, which forms the resistant encrusting material in plant residues.

Fungi are responsible for the majority of lignin decomposition with the mode of attack indicated by the color of the partially decayed substrate, as discussed for the white, brown, and soft rot fungi in the preceding section on carbohydrate decomposition. The most active lignin-degrading fungi, the white rot fungi, degrade the hemicellulose cellulose and the lignin of plant residues to CO_2 and H_2O. Filamentous bacteria such as *Streptomyces* and *Nocardia* as well as other bacteria such as *Pseudomonas* are known to partially degrade lignin. Whether or not they can utilize any of the lignin carbon directly for growth has not been established. It is possible that they attack lignin to remove the barrier sheltering cellulose and hemicelluloses in the plant residues. The penetrating capacity related to fungal and filamentous bacterial growth is important in lignin decomposition.

Only very seldom is a single organism involved in decomposition in nature. Complex interactions occur in cellulose decomposition, but lignin degradation also involves interacting organisms. These are usually fungi. In wood, each individual mycelium tends to occupy discreet zones, which can be differentiated by color differences. In fungi, hyphal interactions are more often antagonistic than mutualistic, yet carbon loss from wood occupied by a number of fungi is nearly always greater than in pure culture studies.

The fungus *P. chrysosporium* is probably the best-studied lignolytic organism. A white rot fungus, it degrades the carbohydrates as well as the lignin of plants and is being studied for potential commercial solubilization of wood for commercial–industrial purposes. This fungus releases two families of extracellular enzymes: lignin peroxidases and manganese peroxidases. Lignin peroxidase is detectable in culture studies only under high O_2 and low available nitrogen, carbon, or sulfur concentrations. It is much more active than manganese peroxide, which is produced on a greater diversity of substrates.

Lignin peroxidase is produced for only a short time in pure culture. Two mechanisms apparently control the time for which lignin peroxidase is active. In culture, it has been found that the genetic transcription of RNA for lignin peroxidase reaches a maximum by day 4 and drops to low levels by day 6. An alternate reason for the decrease in activity is the fact that proteases degrading the lignin peroxidase are found in the medium after day 6. Manganese peroxidase as well as laccase, the other enzyme in lignin breakdown, oxidize only phenolic units of lignin, whereas lignin peroxidase has a broader decomposition spectrum. Because *Phanerochaetes,* the most active lignin decomposer, does not have laccase, its presence is not an absolute requirement for lignin degradation.

Molecular techniques are assisting in the study of lignin decomposition. Genetic probes for the six distinct genomic clones of lignin peroxidase have been produced. Fungal mutants in which nitrogen availability does not control the production of the lignin peroxidase are also available. Therefore, the mode of action and the role in ecology of these organisms should soon be better known.

Lignin solubilization occurs in termite guts. Gut-inhabiting, lignin-solubilizing *Streptomyces* have been shown to oxidatively depolymerize lignin as they degrade the cellulose and hemicellulose of plant residues. The depolymerization produces a water-soluble, acid-precipitable lignin degradation product that is similar to soil humus. The effect of the high pH (9–11) in termite foreguts and the true extent of lignin decomposition rather than just depolymerization and by-product formation are not yet known.

As Fig. 6 shows, the postulated structure of hu-

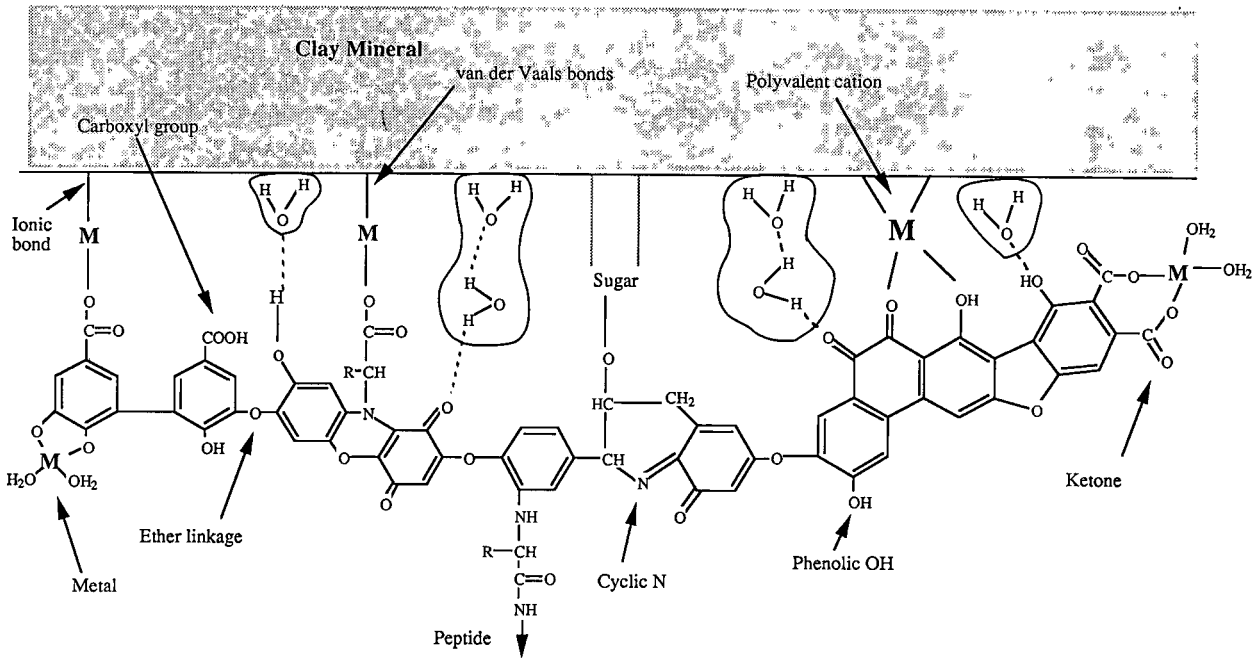

Figure 6 A representative structure of a humus molecule complexed with a clay mineral. [Adapted from Stevenson, F. J. (1982). "Humus Chemistry." John Wiley & Sons, New York.]

mus is similar to lignin in many ways; however, humus is formed by polycondensation of free radicals with amino acids to contain nitrogen, whereas lignin usually does not contain nitrogen. The presence of many different types of bonds, its aromaticity, its three-dimensional configuration, and the production of free radicals during decomposition all lead to slow decomposition rates. However, the major mechanism of inhibiting decomposition is the close relation of humus with soil inorganics, as shown in the interaction with clay in Fig. 6. Modern instrumental methods indicate that humus has fewer phenolic groups (aromaticity) than previously thought. However, the mechanisms of resistance would be similar to those for the structure shown in Fig. 6. This organic matter–clay interaction allows humus to persist in aerobic surface soils for hundreds and even thousands of years and to accumulate until the dominant form of organic carbon in nature. When humus is solubilized by removal from clays and by breakage of the hydrogen bonds that aggregate the otherwise fairly low-molecular weight molecules, it is susceptible to attack by the same microorganisms that are responsible for lignin decomposition.

III. Controls on Organic Matter Decomposition

In addition to the genetic controls of organisms involved in decomposition and the chemical configuration of the substrate itself, a number of nonbiological, abiotic controls affect decomposition. Decomposition is an oxidation process. Often, the most important single factor is the availability of an electron acceptor. This is closely tied to the redox potential and aeration. Water availability, pH, association with inorganic constituents, and the availability of nutrients are other controls.

A. Availability of Electron Acceptors

The type of electron acceptor greatly controls the energy available for decomposition. For example, the oxidation of glucose [$C_6H_{12}O_6$] to CO_2 and water yields seven times as much energy in the presence of O_2 as it does when the sulfite ion is reduced as the electron acceptor. Because of its high affinity for electrons and its requirement in the enzymatic degradation of ligniferous compounds, oxygen is the

preferred electron acceptor. The supply of oxidizable organic compounds, a supply of O_2, some means of removing the CO_2, and the presence of the appropriate enzymes allow aerobic respiration to occur. Because redox potentials can identify both changes in O_2 availability and the presence of other electron acceptors, expression of respiration on the basis of redox potential (Eh) is very worthwhile.

Aerobic soils usually have Eh values between 400 and 600 mV compared to that of O_2 at 800 mV. The transfer of electrons from organic substrates through the electron transport chain with the resultant production of adenosine triphosphate results in the overall processes shown in Fig. 7. This series of diagrams shows the pathways of organic matter decomposition in five zones of redox potential. The restriction of the oxygen supply, by soil depth, high CO_2 contents, or high water contents, results in the cessation of activities by obligate aerobes such as most of the fungi and many of the bacteria. The facultative anaerobic bacteria will then utilize nitrate as an electron acceptor. If this is not available, oxidized manganese, ferric iron, sulfite, other organics, and even CO_2 can act as electron acceptors under appropriate conditions.

The utilization of nitrate as a terminal hydrogen acceptor instead of O_2 in Zone II is called nitrate respiration, or dissimilatory nitrate reduction. This is a significant reaction in decomposition of organic matter; more important, it is a mechanism for the loss of fixed nitrogen from soils and leads to the introduction of N-oxides into the atmosphere. These reactions have major implications in the global climate change problems now receiving so much attention. The reduction of nitrate to N_2 also results in denitrification, but the N_2 , already being the major atmospheric gas, does not have significant effects on either temperature or atmospheric ozone contents. Under highly reducing conditions (Eh < -100 mV), nitrate respiration leads directly to ammonia. The availability of O_2 inhibits denitrification in all cases studied. However, because nitrate is readily soluble in water, it can be moved from aerobic areas such as the interaggregative space in soils to within the anaerobic aggregates. Strong Eh gradients also exist in rice paddies, waste waters, sediments, and peats.

Manganese and iron respiration can be carried out by organisms such as *Bacillus* and *Aerobacter*. These processes are important in soils that are at times water-logged and in aquatic systems where iron- and manganese-reducing bacteria are common.

Fermentative microorganisms, which utilize internally produced simple organic compounds such as electron acceptors, can exist independently, but in nature they more often form complex communities with sulfate reducers. Because of the predominance of sulfate in aquatic systems, especially marine systems, sulfate reduction plays a greater role in organic matter decomposition in these areas than does the utilization of nitrate as an electron acceptor. The fermentative bacteria such as the Enterobacteriaceae or obligate anaerobes such as *Clostridium* bring about mineralization of a range of organic intermediates with the production of CO_2, NH_3, H_2, sulfide, and organic acids or CO_2 and CH_4. Sulfate reduction often is brought about by two genera of strict anaerobes, *Desulfovibrio* and *Desulfotomaculum*. Decomposition of organic matter during sulfate reduction usually does not proceed beyond the level of acetate, which is then a by-product of the reaction.

At Eh values between -200 and -100 mV, methanogenesis involves those strict anaerobes that obtain their energy from coupling the oxidation of a limited range of substrates to the reduction of CO_2 to CH_4. Those organisms producing methane (methanogens) compete for the same energy sources as sulfate reducers, but the sulfate reducers are generally more successful scavengers. Thus, methanogenesis usually starts after sulfate reduction ceases. At Eh values lower than -200 mV, the major *in situ* substrates are acetate and H_2-CO_2. Under some conditions, the majority of the CH_4 produced comes from acetate. In other conditions, CO_2 is the major precursor of the methane. In addition to acetate and H_2-CO_2, formate and methanol have been shown as substrates for methanogenesis. The relative importance of these substrates depends largely on environmental conditions. Lake sediment studies have shown that approximately 70% of the CH_4 originates from acetate. In marine sediments, the major CH_4 precursor was found to be CO_2. [*See* METHANOGENESIS.]

Methane itself contains a great deal of energy. A large proportion of the methane that is produced in anaerobic aquatic areas is reoxidized in the more aerobic water layers above. Surface soils, which are largely aerobic, act as major sinks of methane gas in that they absorb it and soil microorganisms reoxidize it to CO_2. The CH_4 that escapes the biological decomposition cycle enters the air where it is only

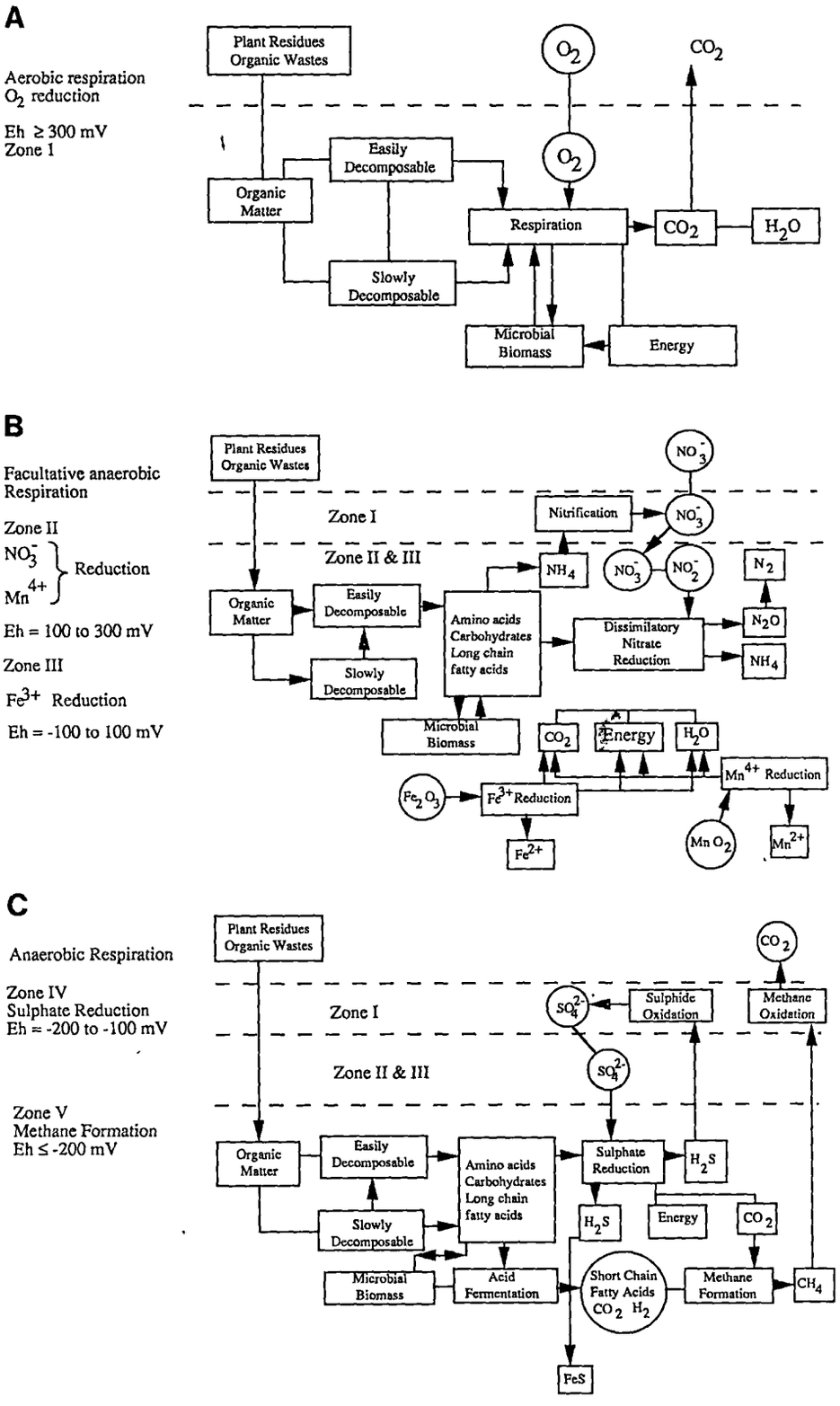

Figure 7 (A) Pathways of organic matter decomposition during aerobic respiration. (B) Pathways of organic matter decomposition during facultative anaerobic respiration. (C) Pathways of organic matter decomposition during anaerobic respiration. [Fig. 7A–C from Reddy, K. R., Feijtel, T. C., and Patrick, W. H. (1986). In Y. Chen, and Y. Avimeloch, eds), "The Role of Soil Organic Matter in Modern Agriculture" pp. 117–168. Martinus Nijhoff, Dordrecht.]

slowly chemically oxidized. It is a much more efficient reflector of infrared radiation than is CO_2 and thus can potentially act as a greenhouse gas. Methane is the most abundant organic gas in the atmosphere at approximately 1.64 ppm. Analysis of gases trapped in ice cores has shown a significant recent rise in the methane concentration of the atmosphere. Table IV shows the annual methane release from identified sources with a range of 344–672 $\times 10^{12}$ g CH_4 being released annually. Rice paddies and natural wetlands are major contributors, but the microbial activities occuring during decomposition of plant materials in ruminants and biomass burning also create significant amounts.

Table IV Estimates of Methane Emissions to the Atmosphere

Source	Range of reported CH_4 emission ($\times 10^{12}$ g yr^{-1})
Rice paddies	70–170
Natural wetlands	40–160
Landfill sites	30–70
Oceans/lakes/other biogenic	15–35
Ruminants	66–90
Termites	2–5
Natural gas losses	30–40
Coal mining	35
Biomass burning	55–100
Other nonbiogenic	1–2
Total	344–672

[Adapted from Schutz and Seiler. (1989). In "Exchange of Trace Gases between Terrestrial Ecosystems and the Atmopshere" (M. O. Andreae and D. S. Schimel), pp. 209–228. John Wiley & Sons, New York.]

B. Moisture, Temperature, and pH Controls

Moisture plays a complex role in that excess moisture limits O_2 diffusion. This results in anaerobiosis and the related redox potentials for waterlogged soils, peats, rice paddies, sediments, and deep O_2-free (anoxic) areas of lakes. Moisture also plays a direct role in controlling decomposition in areas where water availability is limited.

Optimum moisture levels are found after well-aggregated soils have drained for up to 48 hr after a rain or irrigation. The space between the aggregates contains air, but the surface of the aggregates and much of the intraaggregate space contains water films. Productive soils often have a solid, water, and air content of 50, 25, and 25%, respectively. As soils dry out from this optimum there is a complex series of interactions with a slow decline in the capability of microorganisms and their extracellular enzymes to decompose organic matter. Because fungi are more resistant to desiccation than bacteria, they play a greater role under drier conditions. The role of water availability, called moisture stress, has complex effects on populations and the enzymatic reactions of individual organisms.

Temperature also controls decomposition. The easiest way to describe temperature effects is to use the principles established by the Arrhenius equation. The Q_{10} effect, in which a reaction doubles with every 10°C rise in temperature within the appropriate temperature range, also is a useful concept. The general control or organism's activity by temperature must be considered in conjunction with specific optima for psycrophilic, mesophilic, and thermophilic organisms.

Low pH also has controls on decomposition similar to those described in the general microbiology literature. The most easily noticed effects of the interactions of all the controls on decomposition can be seen in the formation and consequent degradation of peats. These are organic soils that build up under excess water. Under waterlogged conditions, anaerobiosis is the major controlling factor; acidic conditions, however, also often develop. Peats are formed in all temperature zones of the earth where plant production is greater than decomposition because decomposition is slowed by lack of an electron acceptor such as O_2. Peats have been shown to accumulate in a range of 0.6–10 cm in height annually; the high accumulation rates occur rarely. Drainage of the flooded areas results in decomposition overtaking production. Subsidence rates of 2.1 cm yr^{-1} have been reported in southern Quebec, Canada. The Netherlands have reported subsidence rates of 1.8 cm and the Sacramento Delta in California and the organic soils of Florida as much as 7.6 cm annually. This subsidence results from the compaction effects of the physical removal of water as well as from decomposition. Subsidence is a major problem where peats are used for agricultural purposes.

IV. Methods of Measuring Decomposition

Measurement of substrate alteration and carbon loss from the substrate have been the traditional methods

for measuring decomposition. The evolution of CO_2 can be measured under both field and laboratory conditions. In pure cultures growing on simple substrates, the total CO_2 evolved is an estimate of decomposition. In nature, there is always a background of more resistant organic materials that are only partially degraded. The subtraction of the CO_2 evolved by an untreated soil from that of the soil plus substrate provided much of the earlier information available in the literature. This measurement is made difficult by the fact that the addition of new substrate often increases the decomposition of the material already present in the soil. Tracer experiments using isotopes of carbon such that the decomposition of the added material can be separated from that occurring naturally are, therefore, often used in measuring decomposition in nature.

In terrestrial systems under aerobic environments, decomposition very nearly equals plant production. Thus, a knowledge of aboveground litter and of root inputs into the soil also provides an estimate of overall decomposition. Where disturbances occur, measurements in the change of the total carbon stored also are meaningful, because these measurements can change significantly when a system is disturbed. In the tropics, total soil organic matter levels can drop to 50% of the original during the first 5–10 yr after clear-cutting or burning. In the prairies of temperate climates, 50–100 yr are necessary to reach a new steady-state level that also approximates 50% of the original level. In each of these terrestrial systems, erosion or the loss of organic matter by wind or water action on the disturbed site also plays a role.

Other methods used in the field are the measurement of plant litter remaining on or near the surface. If the system is in a steady state such as in a mature forest, this can give very meaningful results. The decomposition rate constant can be determined by dividing the annual rate of litter production by the total amount of litter accumulated on the forest floor. The now-classic diagram of Olson, published in 1963 (Fig. 8), shows that decomposition rate constants can be determined by plotting annual litter production versus litter present on the forest floor. These rates can vary by as much as 256-fold. The rate for Ponderosa pine in California is 1/64th the rate for an average tropical forest. Very wet tropics have high litter production rates yet accumulate little litter because of decomposition rates four times those in other tropical soils and 256 times those for Ponderosa pine, which has a resistant litter in a dry enviroment.

Litter decomposition has been studied in many ecosystems by enclosing the litter in mesh bags. This allows comparisons to be made about the effects of different types of materials under field conditions. Weighing the bags removed over a period of time gives an estimate of decomposition. The technique is simple and can be duplicated in many different ecological habitats. Nylon bags with various sizes of mesh allow a measurement of the effect of

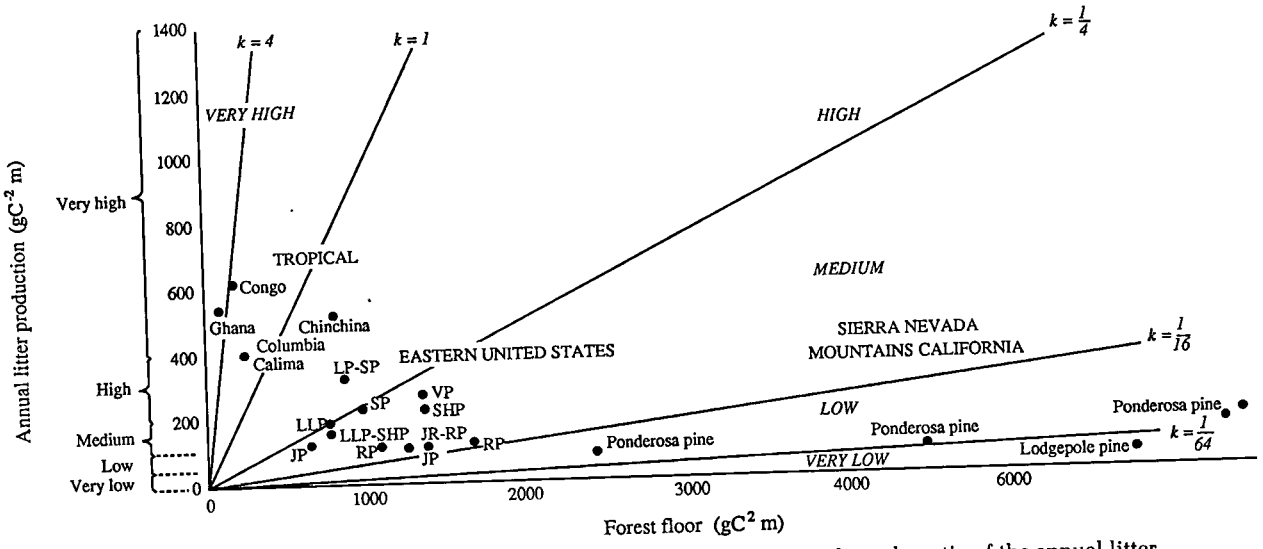

Figure 8 The decomposition rate constant k (yr^{-1}) estimated for evergreen forests from the ratio of the annual litter production to the total litter on the forest floor. [From Olson, J. S. (1963). *Ecology* **44**, 331.]

various soil fauna. The technique does not work well in grasslands or cultivated fields nor does it give actual rates; it is, however, good comparative procedure.

Tracer techniques make it possible to label a specific component under study such that its decomposition can be measure in the presence of an excess of unlabeled materials already present in nature. The carbon isotope ^{14}C, a weak β-emitting radioactive isotope, can be incorporated into plant materials. It is also easily measured, but it is a radioactive isotope. Another isotope of carbon, ^{13}C, is a stable isotope that makes up about 1% of the naturally occurring carbon. Not radioactive, it must be measured by a mass spectrometer, which is more expensive and less sensitive than tracer techniques.

Nitrogen is closely associated with carbon in all living materials. It also is the nutrient that most often limits plant growth. In excess concentrations, this nutrient can cause pollution of both ground water and the atmosphere. Its availability is closely controlled by decomposition and, thus, nitrogen turnover is usually studied relative to organic matter decomposition and, thus, nitrogen turnover is usually studied relative to organic matter decomposition. The only usable isotope available is ^{15}N, which must be measured by the mass spectrometer. As with ^{13}C, this involves larger amounts of tracers and, thus, greater cost. The new automatic mass spectrometers now available, however, have speeded up and lowered the analytical costs to such an extent that ^{15}N and ^{13}C use should not be limited by cost or availability.

Organic materials can be labeled in numerous ways. One can utilize the normal background of ^{14}C in the atmosphere as in the process of carbon dating. The use of fossil fuels, which have been buried so long that they no longer contain ^{14}C, is increasing atmospheric CO_2 and is also lowering the amount of ^{14}C, normally in the atmosphere. This causes problems in carbon dating of more recent organic materials, but it does provide a tracer for research.

Plants differ in the amount of the stable isotope ^{13}C they incorporate. This can be used to follow their decomposition under field conditions. The most common method, however, is to grow the plants in either an enriched ^{14}C or ^{13}C atmosphere, which results in labeling of the above- and underground materials. This can be done in the field using canopies to enclose the CO_2. By incorporating ^{15}N through injection into the stem, the allocation of both carbon and nitrogen in above- and underground plant components can be measured by sampling over a time interval. The decomposition of separate components such as roots, litter, and soil microorganisms can be evaluated. This will be followed by tracer loss from the soil humus as it is, in turn, formed and decomposed over an extended time period. The isotope dilution calculations employed for tracers in experiments such as those preceding are the same regardless of the isotope used.

V. Mathematical Modeling of Decomposition Rates

The number of different chemical constituents in plant residues as well as those in soil organic matter and the effects of all the controls discussed previously make it essential to describe this process with the aid of a computer. This is most easily done with the use of mathematical models of both tracer and nontracer data. Although the reactions involved are complex, they are enzyme-mediated. Decomposition processes follow fairly straightforward kinetics. It has been found that first-order kinetics most often best describe the decomposition of single components in soil or sediments. If substrate C is decomposed with time according to first-order kinetics, the equation describing this decomposition is

$$\frac{dC}{dt} = -kC,$$

where k is the decomposition rate constant controlling the reaction. Solving the preceding equation produces

$$Ct = C_0 e^{-kt},$$

where Ct is the substrate remaining at any time t and C_0 is the substrate present at zero time. The first-order rate constant k is some expression of unit time. Depending on the speed of decomposition, it can be hr^{-1}, day^{-1}, or even yr^{-1}. First-order reactions are logarithmic functions. By dividing through by C_0 and taking the natural log (ln) of both sides, we obtain

$$\ln Ct/C_0 = -kt.$$

A plot of $\ln Ct/C_0$ yields a straight line with a slope of $-k$.

It is difficult to envision the decomposition rate because its units are time^{-1}, indicating that it is independent of substrate or product concentrations. The concepts of half-life and turnover times make it somewhat easier to envision the process. The half-life is described as the time at which one-half of the substrate is still present—for example,

$$C_t = C_0/2$$

because the functions are logarithmic:

$$\ln\left(\frac{C_0/2}{C_0}\right) = -kt_{1/2},$$

which is $t_{1/2}$ (or the half-life) $= 0.693/k$.

At steady state, the turnover time (t) of this reaction is the time required to decompose an amount equivalent to the original amount (C_0). This is $-1/k$, where k is expressed in yr^{-1}, days^{-1}, etc. This concept was used in Fig. 8, where decomposition rates for various forest-type–climate interations are shown.

Plant and microbial residues are comprised of a number of constituents. Thier decomposition is, therefore, best described as the sum of the number of first-order reactions. In addition, microbial growth incorporates carbon into new cell constituents and forms waste products. Figure 9 shows the accumulation as well as the decay of micobial products relative to the total carbon remaining during a period of decomposition, the difference having been evolved as CO_2. It also shows that the sum of the number of first-order reactions gives a great deal of information—the original amount of each of the components as well as the associated decomposition rates.

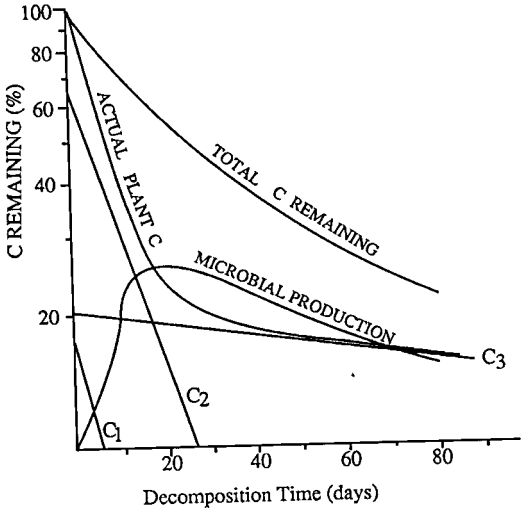

Figure 9 Decomposition of the carbon (C) to plant residues after correction for microbial growth. Equation for actual decomposition:

$$C = C_1 e^{k1t} + C_2 e^{k2t} + C_3 e^{k3t} = 15e^{-0.2t} + 65 e^{-0.08t} + 20e^{-0.01t}.$$

Substraction of microbial products from the total carbon remaining results in the curve shown for actual plant carbon in Fig. 9. The decomposition rate constants shown in Fig. 9 represent the three major groups of plant constituents described earlier. The labile carbon, C_1, is present at 15% and has a k of -0.21 days. Representing cellulose and hemicellulose, C_2 is present initially at 65% with a k of -0.08 days. Lignin, C_3 is present at 20% with a k of -0.01 days. The half-life for lignin is

$$\frac{0.693}{k} = \frac{0.633}{0.01} = 69 \text{ days.}$$

The turnover time, as described previously, is

$$\frac{1}{k} = \frac{1}{0.01} = 100 \text{ days.}$$

The abiotic controls such as temperature, moisture, clay content, and mixing slow down decomposition from its maximum. These controls can be expressed in mathematical modeling as functions that lower the decomposition rate (k) under field conditions. The model incorporates the plant residue designations and the decomposition rates shown in Table III and Fig. 10. Plant residues consisting of three fractions, C_1, C_2, and C_3, are attacked by microorganisms and, to some extent, by soil fauna. These form microbial biomass. A portion of the resistant fraction (C_3) is not decomposed and enters the slow plant and microbial by-products pool. This pool, together with the microbial biomass, turns over fairly rapidly and provides the basis for the release of considerable carbon and much of the nitrogen. Some of the resistant plant material can interact with the plant and microbial by-products or be stabilized in aggregates. These reside in soil for periods of up to 25–50 yr.

A portion of the organic matter becomes very chemically resistant and is incorporated into stable aggregates. This material has been shown by carbon-dating techniques to last for thousands of years in

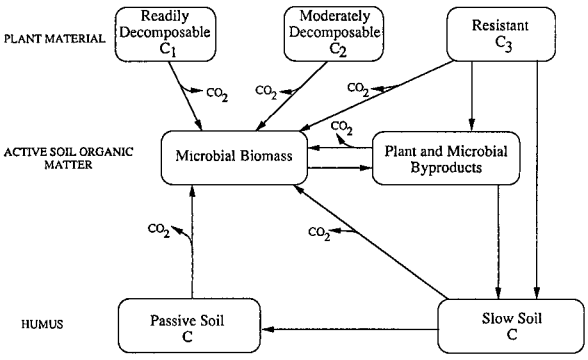

Figure 10 Model showing decomposition of plant materials and the formation of active soil organic matter and soil humus.

aerobic soil. The buildup of soil materials that are resistant to decomposition is the basis of life on this earth because it means that nutrients in the soil organic matter are only slowly released. The organic matter also gives the soil the necessary structure, aeration, and chemical characteristics necessary for plant development and growth.

A model such as the previous one has been used to describe the decomposition of straw under a number of environmental conditions. Table V shows that in the laboratory, straw has a decomposition rate (k) of 0.08 days^{-1}. This is a turnover time of 12 days. The turnover time of the same straw in a Canadian field where both drought and cold slowed down decomposition, however, was 330 days. A comparison of Table V with Fig. 8 shows the similarities between the two. Figure 8 represents field measurements of steady-state conditions of litter with different compositions undergoing decomposition under a wide variety of conditions. Table V is determined from a mathematical model of readily decomposable substrate incorporated into the soil where steady-state conditions did not apply. Thus, ^{14}C tracer techniques were used. Figure 8 is derived from forests in steady-state conditions and did not require tracers. Both assume first-order kinetics and give comparable results that tell us a great deal about decomposition under a wide variety of conditions.

VI. The Application of Our Knowledge of Decomposition

We now have fairly good knowledge about the substrates of decomposition and how they affect decomposition rates. The organisms involved require further elucidation, but the major types are probably known. The biochemistry of the process requires further definition, especially in the case of lignin and soil humus. The application of molecular genetics should give us an understanding of the genetic controls and also allow for a better understanding of the types of organisms involved in these complex reactions. Field measurements and modeling have provided us with an understanding of the abiotic controls, allowing us to validate our hypothesis about this important process.

The utilization of information on decomposition has, however, just begun. We must now take the information we have obtained and use it to gain a better understanding of how decomposition fits into general ecosystem functioning. We can also use our knowledge about decomposition to help improve our way of life and the environment. An understanding of decomposition will allow us to better control plant residue breakdown rates so that the nutrients released during the decomposition of plant residues are efficiently utilized by new plant growth. Decomposition often occurs when plant growth is at a minimum. This results in a loss of plant nutrients and pollution of both the atmosphere and ground water.

Decomposition can be managed to help degrade the large number of human and farm animal wastes and the industrial chemicals that are now polluting the environment. Studies on the enzymes and organisms involved should allow us to transform products of agriculture and forestry into fuels and chemicals.

Table V Effect of Environment on Decomposition Rate of Plant Residues Added to the Soil

Residue	Turnover time (days)	k (days^{-1})	Relative rate
Wheat straw, laboratory	12	0.08	1
Rye straw, Nigeria	25	0.04	0.5
Rye straw, England	100	0.01	0.125
Wheat straw, Saskatoon	330	0.003	0.05

The current rapid use of coal and oil by humans is returning to the atmosphere, over a very short time period, plant and animal residues that escaped decomposition millions of years ago during geological time. This can potentially cause major global climatic changes. We must find ways to overcome this imbalance in nature and to turn its effects into positive ones such as more plant growth where desired and a larger store of soil organic matter.

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